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NO_x CONTROL

TECHNICAL FIELD

The present disclosure relates to NO_x controls.

BACKGROUND

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5 The reduction of nitrogen oxide (NO_x), e.g., nitric oxide (NO), nitrogen dioxide (NO₂), and nitrous oxide (N₂O), in exhaust gas is a widely addressed problem as a result of environmental concerns and mandated government emissions regulations, particularly in the transportation industry. One approach uses three-way conversion catalysts to treat the exhaust gases of spark-ignited gasoline internal combustion engines for the reduction of NO_x emission, since the exhaust contains minimal oxygen.

10 However, fuel economy and global carbon dioxide (CO₂) emission concerns have made it desirable to operate engines under lean-burn conditions to realize a benefit in fuel economy. Under such conditions, the exhaust streams contain excessive oxygen, and accordingly, conventional three-
15 way conversion catalysts are generally inefficient in the reduction of nitrogen oxides. For example, a lean burn engine exhaust stream has from about 1% to 10% excess oxygen relative to the amount of fuel. Further, exhaust streams of compression-ignition engines such as diesel engines also have high oxygen content. For example, the exhaust stream may contain from perhaps about 2-20
20 molar% oxygen based on the total exhaust, and, in addition, contains a significant amount of particulate emissions.

Hydrocarbon (HC), particulate, or NO_x emissions from an exhaust or effluent stream may be treated with a non-thermal plasma reaction in conjunction with a NO_x catalyst, adsorber, or storage compound. Typically, the
25 various NO_x compounds are converted to NO₂, which, in the presence of HCs

and water, is converted into nitrogen gas (N_2), oxygen gas (O_2), carbon dioxide (CO_2).

In addition to the NO_x , the exhaust gases typically contain sulfur compounds such as sulfur dioxide (SO_2) gas and particulate sulfate (SO_4), which are produced by the burning of sulfur contained in the fuel. The NO_x catalyst oxidizes SO_2 to sulfur trioxide (SO_3) in oxygen-rich atmospheres. Still further, SO_3 reacts readily with water vapor, which is also contained in the exhaust gases, to produce sulfite ions and sulfate ions. The sulfite ions and sulfate ions react with the NO_x catalyst to produce sulfites and sulfates. The resulting sulfites and sulfates adversely affect the NO_x storage reaction. Thus, such sulfites and sulfates are commonly referred to as NO_x poisons.

Therefore, as is apparent from the above brief description of NO_x removal, such NO_x poisons result in degraded exhaust purification. What is needed in the art is a sulfur resistant NO_x catalyst.

SUMMARY

The above-described and other disadvantages of the prior art are overcome by the system wherein a NO_x control for an exhaust is provided. The NO_x control includes a nickel compound in conjunction with a NO_x adsorber. The NO_x adsorber is generally suitable for a high oxygen content exhaust, such as an exhaust having oxygen content greater than about 1 molar% based on the total exhaust.

Further, a system for treating an exhaust gas includes a non-thermal plasma reactor and a NO_x control. The NO_x control includes a nickel compound in conjunction with a NO_x adsorber, which is generally suitable for a high oxygen content exhaust, such as an exhaust having oxygen content greater than about 1 molar% based on the total exhaust.

Still further, a system may also contain a first non-thermal plasma reactor, a particulate trap, a second non-thermal plasma reactor, and a NO_x control.

A method for poison protection in an engine exhaust is also provided, wherein an exhaust gas is exposed to a NO_x control which includes a

nickel compound in conjunction with a NO_x adsorber, which is generally suitable for a high oxygen content exhaust, such as an exhaust having oxygen content greater than about 1 molar% based on the total exhaust. The exhaust gas for this method typically contains greater than about 1 molar% oxygen based on the total exhaust.

Further, methods for forming a NO_x control are also described, comprising either mixing, milling, or sintering a nickel compound integrally with a NO_x adsorber, or processing a nickel compound with a NO_x adsorber by mixing, milling, or sintering, washcoating, imbibing, impregnating, physisorbing, chemisorbing, precipitating, vapor depositing, or any combination of at least one of the foregoing processing techniques.

BRIEF DESCRIPTION OF THE DRAWINGS

For a further understanding of the nature of the present invention, as well as other features and advantages thereof, reference should be made to the following detailed description taken in conjunction with the accompanying drawings, which are meant to be exemplary not limiting, and wherein like elements are numbered alike in the several figures.

Figure 1 is a schematic of a NO_x reduction system.

Figure 2 is a schematic of another NO_x reduction system.

DESCRIPTION OF THE PREFERRED EMBODIMENT

A NO_x adsorber or a NO_x adsorber system comprises a nickel or nickel oxide (NiO) component as a protective portion to minimize poisoning of the NO_x adsorber material or the NO_x adsorber by sulfur compounds.

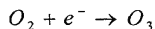
Referring now to Figure 1, a schematic of a NO_x reduction system 10 is detailed. The NO_x reduction system 10 includes a non-thermal plasma reactor 14 that receives a contaminated exhaust 16, for example, from a spark-ignition or compression-ignition engine 12. The contaminated exhaust typically comprises oxygen, HCs, NO_x, and possibly other contaminants including, but not limited to, sulfur compounds (e.g., SO₂, SO₄) and particulate

carbon. Under oxidizing conditions, the contaminated exhaust 16 may comprise about 1% to about 20%, or even up to about 30%, oxygen.

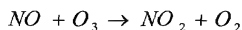
The non-thermal plasma reactor 14 generally converts the various NO_x compounds into NO₂. A partially cleaned gas stream 18 exits the plasma reactor 12 and is introduced into a NO_x control 20 generally for decomposing HCs and NO_x into O₂, CO₂, H₂O, and N₂ with clean exhaust 22 exiting the NO_x control 20.

Plasma reactor 14 is capable of generating a potential for ionizing gasses. The plasma reactor 14 is typically connected to a power supply and comprises system for generating a non-thermal plasma. The plasma includes a mixture of reactive free radicals, ions, and electrons that cause conversion or partial conversion of HCs, oxygen, and certain NO_x compositions, as well as neutral species.

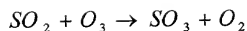
A non-thermal plasma can be generated between a pair of electrodes by a number of methods, including electrical fields, electron beams, and irradiation with electromagnetic energy of appropriate intensity and wavelength. Electrical field plasma can be generated with a high voltage (e.g., about 10,000 volts) electrical field suitable for the gas and gap geometry. A local dissociation of electrons results, and the electrons accelerate rapidly in the electrical field. The accelerating electrons strike and ionize other molecules. If the voltage is stopped before or shortly after a streamer (equivalent to the path of ionized molecules and electrons) crosses the gas gap causing an arc discharge, then a non-thermal plasma of ions and free electrons is formed. For example, oxygen gas (O₂) is ionized into ozone (O₃) according to the following reaction:



The NO_x components, particularly nitric oxide, react in the presence of ozone as follows:



Further, due to the ozone, some of the SO₂ present is converted to SO₃ generally as follows:



Certain configurations for the plasma reactor 14 include that of a dielectric barrier reactor, an electrified packed bed reactor, a glow-discharge plasma reactor, a corona discharge reactor, and other suitable plasma reactors. In the various plasma reactor types and geometries, the discharges that create the plasma originate at the surface of the electrodes at a point where the peak electric field strength is at least about five times that of the average energy field (a discharge point). Thus, preferably the reactor has a sufficient number of such discharge points positioned so as to substantially uniformly treat the target emissions in the exhaust stream.

For example, when employing a dielectric barrier reactor s plasma reactor 14, one or both electrodes are coated with a dielectric material, e.g., flat alumina plates screen printed with a dielectric such as a copper chrome alloy ink coating. During operation, a streamer is formed by an electron accelerating in the electric field, with the streamer extinguished on the surface of the dielectric material. From the plasma reactor 14, the exhaust enters NO_x control 20. NO_x control 20, which is particularly suited for oxidized exhausts having oxygen content of greater than 1, 2, 5, 10, 20, or even 30 molar% based on the total exhaust (wherein the oxidized exhaust comprises greater than 1% oxygen is referenced as "high oxygen content"), comprises a nickel compound and a NO_x active material such as a NO_x adsorber. The nickel compound, which may comprise a brick, or a mixture such as a coating or an integral mixture on the NO_x adsorber, can comprise pure nickel oxide (NiO) or a mixture, alloy, composite, or cermet of NiO and metals, metal oxides, ceramics, binders, fugitive materials, combinations thereof, and the like. Some possible materials which can be combined with the NiO include copper oxide, silver oxide, chrome oxide, as well as mixtures, alloys, composites, and cermets comprising at least one of the foregoing materials.

The nickel compound can comprise about 1 weight percent (wt.%) to about 100 wt% NiO, preferably about 50 wt% to about 100 wt% NiO,

and more preferably about 80 wt% to about 100 wt% NiO, based on the total weight of the nickel compound.

The compound composition is provided in various forms during manufacture, including: solid, for processes such as mixing, milling, or
5 sintering, and the like; liquid solution, for processes such as washcoating, imbibing, impregnating, physisorbing, chemisorbing, precipitating, and the like; gaseous composition, for processes such as vapor depositing, and the like; or any combination of phases.

In one embodiment, a nickel compound coating is formed on a
10 support material independent from the NO_x catalyst material, generally in sufficient quantity to promote reduction of NO_x poisonous species. For most automotive applications, a sufficient quantity of nickel compound is about 0.125 milligrams per square centimeter (mg/cm²) to about 0.512 mg/cm², with about 0.256 mg/cm² to about 0.384 mg/cm² of nickel compound preferred. The
15 coating composition may be mixed, milled, sintered, washcoated, imbibed, impregnated, physisorbed, chemisorbed, precipitated, vapor deposited, otherwise applied, or processed by any combination of at least one of the foregoing processing techniques, integrally with the support material.

The support material can comprise any material: designed for use
20 in a spark-ignition or compression-ignition environment (e.g., temperature of about -40°C to about 1,000°C; capable of withstanding exposure to HCs, nitrogen oxides, carbon monoxide, carbon dioxide, carbonaceous soot, and/or sulfur; and having sufficient surface area and structural integrity to support the desired coating composition. Preferably, the support material has a surface area
25 up to or exceeding about 600 squared meters per gram (m²/g). Some possible support materials include, but are not limited to, alumina (e.g., gamma-alumina, delta-alumina, theta-alumina, and the like), zeolite, zirconium, cerium, cesium, magnesium, titanium, silicon, cordierite, silicon carbide, porous glasses, metallic foils, mullite, alkali and alkaline-earth zirconium phosphates (NZP),
30 and combinations, alloys, oxides, and cermets comprising at least one of these materials, among others.

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Although the support materials can have any size or geometry, the size and geometry are preferably chosen to optimize surface area in the given design parameters. Suitable support materials are in the form of mesh, corrugated foils, layered materials, spun fibers, extrudates, spheres, beads, tablets, ceramic foams, and monoliths. In one embodiment, the support material comprises a monolith (ceramic or metallic) having a honeycomb geometry, with the combs through-channel having any multi-sided or rounded shape, with substantially square, triangular, pentagonal, hexagonal, heptagonal, or octagonal or similar geometries preferred due to ease of manufacturing and increased surface area.

In addition to formation on a support material, the nickel compound may be provided as a self supported structure suitable for placement within a gas stream. For example, a nickel compound may be formed into a brick or a porous compact which forms at least a portion of the NO_x control

Although the nickel compound is preferably employed in a NO_x control 20 disposed upstream of the NO_x adsorber, the nickel compound can be employed integrally with the NO_x adsorber. The nickel compound may be mixed, milled, sintered, washcoated, imbibed, impregnated, physisorbed, chemisorbed, precipitated, vapor deposited, otherwise applied, or processed by any combination of at least one of the foregoing processing techniques with the NO_x adsorber. Preferably, the NO_x control 20 is formed by adding the nickel compound to the NO_x adsorber in a manner so as not to occupy active sites intended for NO_x reduction. The protective nickel compound coating acts as a poison trap, generally preventing or minimizing the possibility of sulfur and other contaminants occupying or otherwise deactivating the NO_x catalyst material.

The NO_x adsorber may comprise one or more catalyst materials integral with a support material, such as those described above for supporting the nickel compound. Possible NO_x catalysts comprise those materials capable of reducing NO_x to N₂ and various oxygen containing compounds (e.g., CO₂, H₂O, and the like). For example, these materials include cesium, barium, lanthanum, silver, zirconium, zeolites, alumina, silicon, manganese, as well as

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alloys, oxides, and combinations comprising at least one of the foregoing materials. Further, the NO_x catalyst system preferably comprises a material active in an oxygen rich environment including lean burn spark-ignition engines, or compression-ignition engines such as diesel engines. Such oxygen rich environments may comprise exhaust streams including up to about 30% oxygen. Additionally, the NO_x catalyst system preferably comprises a material active in temperature ranges less than about 500°C, and more preferably active in temperature ranges less than about 150°C (i.e., the light-off temperature).

Referring now to Figure 2, a NO_x reduction system 50 is detailed. The NO_x reduction system 50 includes a first non-thermal plasma reactor 54 that receives a high oxygen content contaminated exhaust 56, for example, from a spark-ignition or compression-ignition engine 52. The contaminated exhaust typically comprises oxygen, HCs, NO_x, and other contaminants including but not limited to sulfur compounds (e.g., SO₂, SO₄) and particulate carbon. The first plasma reactor 54 partially or completely converts HCs, NO to NO₂, oxygen to ozone, among other ionizations, resulting in a partially cleaned exhaust 58 that is introduced to a particle trap 60. Within particle trap 60, carbonaceous and sulfate particles are trapped. Some of the carbonaceous particles react with a portion of the NO₂ to form carbon monoxide (CO) and reconvert NO₂ to NO, which exit in an exhaust 62. The exhaust 62, generally comprising oxygen, ozone, HCs, NO, and NO₂, is fed into a second plasma reactor 66, where NO is converted to NO₂. The exhaust 68, generally comprising oxygen, ozone, HCs, and NO₂, is converted in a NO_x control 20 to water, oxygen, molecular nitrogen, and carbon dioxide which exits NO_x control 20 as clean exhaust 72.

In use, NO_x compounds are converted and adsorbed in sites on the NO_x adsorber. Further, the nickel compound attracts sulfur, as described further herein. Therefore, the NO_x control 20 may be operatively coupled to a desorbing mechanism (not shown) for extended usage. In certain systems, the temperature levels rise sufficiently for nickel to release sulfur compounds and for NO_x compounds to release from the NO_x adsorber (e.g., about 500°C), thus the NO_x control 20 may passively desorb. In other systems, for example,

wherein the temperature levels do not rise above 500°C, desorption may be accomplished by an active mechanism. The active desorption mechanism may comprise heat, a plasma reactor, or other suitable desorption mechanism.

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EXAMPLES

The following examples illustrate specific NO_x controls. It should be understood that the examples are given for the purpose of illustration and are not intended as limitations. In the examples, all parts and percentages are by weight based on the total weight of the composition unless otherwise specified.

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Example 1

Zeolite with a silica to alumina ratio of 5 was triple exchanged with barium nitrate, wherein each calcining step was at 740°C for 2 hours. The resulting mixed oxide was about 18 wt% barium. The barium-zeolite was mixed with nickel 2-ethyl hexanoate, and calcined at 500°C. The result was a stabilized barium-zeolite (Ba-Si₂O₃/Al₂O₃) encapsulated in a poison protective layer of NiO. The nickel oxide-barium-zeolite was dispersed with water containing 2 wt% nitric acid, and the resulting slurry was coated on a 600 cells per cubed inch (cell/in³) cordierite monolith. The wash-coated monolith was calcined at 500°C for 2 hours.

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Example 2

Zeolite was triple exchanged with barium nitrate as in Example 1. About 80 wt% barium-zeolite was mixed with about 20 wt% nickel oxide. The nickel oxide had a surface area of at least about 100 m²/g. The nickel oxide-barium-zeolite was dispersed with water containing 2 wt% nitric acid, and the resulting slurry was coated on a 600 cell/in³ cordierite monolith. The wash-coated monolith was calcined at 500°C for 2 hours.

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Example 3

A first 600 cell/in³ cordierite monolith of a two monolith system was coated with 100 wt% nickel oxide having a surface area of at least 100 m²/g. The coated first monolith was calcined at 500°C for 2 hours. A second
 5 600 cell/in³ cordierite monolith of the two monolith system was coated with composition of zeolite triple exchanged with barium nitrate (as in Example 1).

Example 4

A first layer of a dual layer washcoat was zeolite triple
 10 exchanged with barium nitrate as in Example 1, which was coated on a 600 cell/in³ cordierite monolith. A second layer of the dual layer washcoat system was 100 wt% nickel oxide having a surface area of at least 100 m²/g, which was coated over the first layer on the monolith. The dual layer washcoated monolith was calcined at 500°C for 2 hours.

Example 5

Zeolite was triple exchanged with barium nitrate as in Example
 1. The barium-zeolite was mixed with nickel 2-ethyl hexanoate. The resulting mixture was calcined at 500°C. The result was a stabilized barium-zeolite (Ba-
 20 Si₂O₃/Al₂O₃) encapsulated with a poison protective layer of NiO. About 70 wt% nickel oxide-barium-zeolite and 30% gamma-alumina was dispersed with water containing 2 wt% nitric acid. The resulting slurry was coated on a 600 cell/in³ cordierite monolith. The wash-coated monolith was calcined at 500°C for 2 hours.

Example 6

Zeolite was triple exchanged with barium nitrate as in Example
 1. About 60 wt% barium-zeolite was mixed with 15 wt% nickel oxide having a surface area of at least 100 m²/g and 25 wt% gamma alumina. The nickel
 30 oxide-barium-zeolite-alumina was dispersed with water containing 2 wt% nitric acid, and the resulting slurry was coated on a 600 cell/in³ cordierite monolith. The wash-coated monolith was calcined at 500°C for 2 hours.

Example 7

A first 600 cell/in³ cordierite monolith of a two monolith system was coated with 100 wt% nickel oxide having a surface area of at least 100 m²/g and calcined at 500°C for 2 hours. A second 600 cell/in³ cordierite monolith of a two monolith system was coated with 75 wt% barium-zeolite and 25 wt% gamma alumina. The monolith was calcined at 500°C for 2 hours.

Example 8

A first layer of a dual layer washcoat included 75 wt% zeolite and 25 wt% alumina, which was coated on a 600 cell/in³ cordierite monolith. The coated monolith was calcined at 500°C for 2 hours. A second layer of a dual layer washcoat system included 100 wt% nickel oxide having a surface area of at least 100 m²/g that was coated over the first layer on the monolith. The dual layer washcoated monolith was calcined at 500°C for 2 hours.

Example 9

Barium oxide was mixed with nickel 2-ethyl hexanoate, and calcined at 500°C. The result was barium oxide encapsulated with a poison protective layer of NiO. The nickel oxide-barium oxide was dispersed with water containing 2 wt% nitric acid, and the resulting slurry was coated on a 600 cell/in³ cordierite monolith. The wash-coated monolith was calcined at 700°C for 2 hours.

Example 10

About 80 wt% barium oxide was mixed with 20 wt% nickel oxide having a surface area of at least 100 m²/g. The nickel oxide-barium-oxide was dispersed with water containing 2 wt% nitric acid, and the resulting slurry was coated on a 600 cell/in³ cordierite monolith. The wash-coated monolith was calcined at 700°C for 2 hours.

Example 11

A first 600 cell/in³ cordierite monolith of a two monolith system was coated with 100 wt% nickel oxide having a surface area of at least 100 m²/g. The coated first monolith was calcined at 500°C for 2 hours. The second

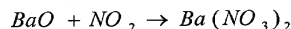
5 600 cell/in³ cordierite monolith of the two monolith system included 100 wt% barium oxide. The coated second monolith was calcined at 740°C for 2 hours.

Example 12

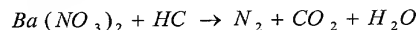
A first layer of a dual layer washcoat comprising 100 wt% barium oxide was coated on a 600 cell/in³ cordierite monolith. The coated monolith was calcined at 740°C for 2 hours. A second layer of a dual layer washcoat system included 100 wt% nickel oxide having a surface area of at least 100 m²/g that was coated over the first layer on the monolith. The dual

10 layer washcoated monolith was calcined at 500°C for 2 hours

In a typical system not including the nickel composition poison trap, a NO_x catalyst system include barium impregnated zeolite. In oxygen rich environments, barium oxide is formed, which generally reacts with NO₂ to form barium nitrate, as follows:

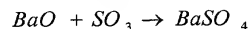


Barium nitrate reacts with the existing HCs, resulting in water, elemental nitrogen, and carbon dioxide as follows:



However, in the presence of sulfur trioxide (SO₃), barium oxide also typically

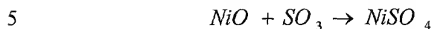
25 reacts to form barium sulfate:



The formation of barium sulfate (BaSO₄) is typically irreversible in systems operating at less than about 500°C. Thus, the NO_x activity correspondingly decreases.

The inclusion of the nickel compound poison trap causes the sulfur trioxide to react with nickel (or NiO), rather than the barium (or other

catalyst) composition. The nickel compositions used preferably have a strong affinity for sulfates. Particularly, NiO reacts readily with sulfur trioxide, which is generally formed due to reaction of ozone and sulfur dioxide as described above. Sulfur trioxide is reacted as follows at the nickel coating trap:



In exhaust systems that have a low oxygen content (e.g., less than about 1 molar% based on the total exhaust), nickel compounds are typically avoided or used in small quantities, e.g., less than about 2 wt.%. The lack of oxygen causes adverse poisoning of the NO_x adsorber. Generally, in neutral or reducing conditions, the nickel oxide will minimally release trapped sulfur. Also, in high temperature environments, the high temperature will decrease the active surface area of the nickel oxide, but the benefits of the nickel oxide described herein are essentially unaffected up to about 800°C. Higher temperatures will further cause irreversible formation of NiAl₂O₄ or other inactive compounds. Furthermore, use of nickel compounds with conversion catalysts employing precious metals such as platinum, palladium, and rhodium may coat the surface of the precious metal, thus such usage is preferably minimized to reduce waste of such precious metal compounds.

Consequently, nickel compounds, provided either separate from or in combination with a support or a catalyst, provides several benefits to typical exhaust systems. One primary benefit is the trapping of poisons (i.e., constituents that may be detrimental to the life of the catalysts or that may bypass catalyst conversion) such as phosphorous, sulfur, halogens, silicon, and other poisons. Further, nickel compounds, particularly NiO, may have NO_x reduction activity; may facilitate organic decomposition by dehydrogenating organics (e.g., dehydrogenating butane to more reactive organics such as butene) and by cracking heavy organics into more reactive lighter organics; and may reduce the amount of sulfated particulates.

While preferred embodiments have been shown and described, various modifications and substitutions may be made thereto without departing from the spirit and scope of the invention. Accordingly, it is to be understood

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that the system and method have been described by way of illustration only, and such illustrations and embodiments as have been disclosed herein are not to be construed as limiting to the claims.

What is claimed is:

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